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Ultrasound Extractions

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Introduction

Sound is transmitted through a medium by inducing vibrational motion of the molecules forming part of it. Human hearing threshold is reached when the frequency of sound is higher than 16–18 kHz. Ultrasound comprises the region of frequencies between 18 kHz and 100 MHz, the upper limit not being sharply defined (**Figure 1**). This broad region can still be divided into two different regions: power ultrasound between 20 and 100 kHz and diagnostic ultrasound between 1 and 10 MHz. The above classification relies on the capability of energy transmission into the medium at the lower frequencies, which induces the cavitation phenomenon.

Relevant applications of ultrasonic energy include its use in animal communications (e.g. bat navigation and dog whistles), medicine for fetal imaging, underwater range finding (SONAR) and nondestructive testing for metal flaws. Recently, ultrasound has also been considered a potential source for enhancement of chemical reactivity. A large variety of chemical and industrial processes rely on high intensity ultrasonication, e.g., cleaning, drilling, soldering, acceleration of chemical reactions, emulsification, sterilization, flotation, homogenization, dissolution, deaggregation of powder, disruption of biological cells, extraction, crystallization, oxidation, etc. A further advantage of the above-mentioned ultrasound-assisted processes is the relative simplicity of both method development and instrumentation.

A brief description of ultrasound fundamentals as well as a discussion of its applications for solid–liquid extraction is given below.

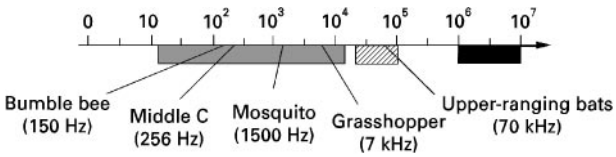

Figure 1 Sound frequencies (Hz, cycles per second). ▩, human hearing 16 Hz–16 kHz; ▨, power 20 kHz–100 kHz (clearing plastic welding sonochemistry); ■, high frequency 1 MHz–10 MHz (medical diagnosis, chemical analysis). (From Mason TJ (1991).)

Fundamental Features of Ultrasound

Vibrations Induced by Ultrasound

Sound waves are usually represented as a series of vertical lines, with intensity being related to separation between them, or as a sine wave where intensity is related to the amplitude (**Figure 2**).

Ultrasonic irradiation of a liquid medium gives rise to an acoustic pressure (P_a) which is added to the hydrostatic pressure (P_h) which exists in the medium. The acoustic pressure depends on time according to the following expression:

$$P_a = P_A \sin 2\pi ft$$

where f is the frequency of the wave (> 16 kHz), t is the time and P_A is the maximum pressure amplitude of the wave. At the point where the lines are close to each other, pressure is higher than normal (i.e. compression region), whereas at the point where the lines are furthest apart, pressure is lower than normal (i.e. rarefaction region).

The intensity of the wave can be defined as the energy transmitted per second per cm^2 of fluid and can be related to P_A as follows:

$$I = P_A^2(2\rho c)^{-1}$$

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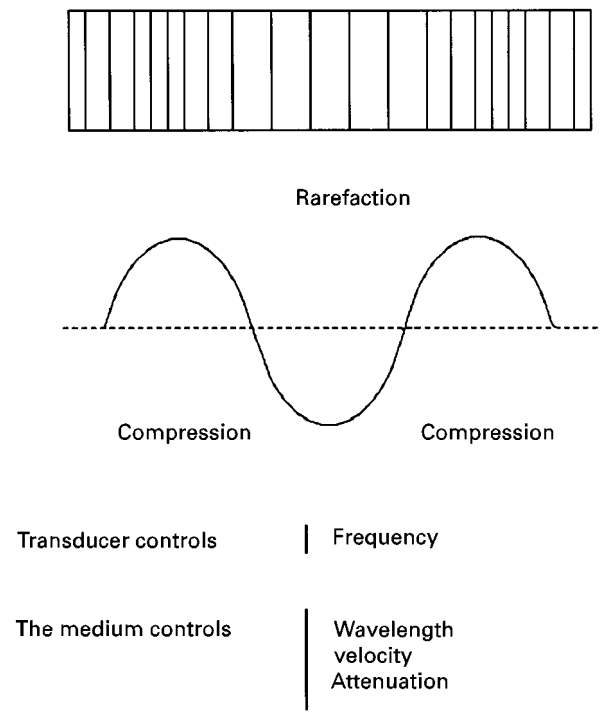

Figure 2 Sound motion in a liquid medium.

where c is the velocity of sound in the medium and ρ is the density of the medium.

Attenuation of Sound in a Liquid Medium

The intensity of the ultrasonic wave decreases with increasing penetration into the medium. Molecular vibration induced by the sound wave results in loss of intensity of the wave, which is transformed into heat. Heating occurs in the sites of compression and cooling at the sites of rarefaction. Since the compressibility of liquids is small, there is little heating caused by ultrasound as waves pass through the medium. The heating effect is caused by the degradation of acoustic energy due to absorption, following the equation:

$$I = I_o \exp(-2\alpha d)$$

where I is the intensity at distance d from the ultrasound source and α is the absorption coefficient.

The Phenomenon of Cavitation

The pressure wave caused by ultrasound transmitted in a liquid medium will, in turn, cause an oscillation of the molecules around their mean position. When a large negative pressure (P_c) is applied to the liquid, where P_c (rarefaction pressure) $= P_a - P_h$, the distance between molecules can overcome a critical distance R, under which the liquid breaks down so that cavitation bubbles form. The R distance for water is around 10^{-8} cm and the pressure involved is 10.1×10^5 kPa, where $P_c = 2\sigma/R$, σ is the surface tension. The cavitation process can be observed at much lower negative pressure (e.g. 10.1×10^4 kPa), as a result of the presence of gas nuclei as dissolved gas, suspended gas bubbles, or gas bubbles caused by heat fluctuations within the liquid. The cavitation threshold decreases with degassed liquids or as consequence of the increase in hydrostatic pressure.

Cavitation can be divided into two classes: transient and stable. Stable cavities oscillate around some equilibrium size (R_0) over several rarefaction–compression cycles. In contrast, transient cavities usually exist over one acoustic cycle, increasing their size during the cycle and collapsing into smaller bubbles. The time required for a bubble to collapse is usually shorter than the period of the acoustic wave, and therefore P_m (i.e. pressure in the liquid at the moment of transient collapse, $P_m = P_h + P_a$) can be considered as constant during collapse. This time can be expressed as:

$$t = 0.915 R_m (\rho/P_m)^{1/2}$$

where R_m is the radius of the cavity at the moment of collapse.

Temperatures and pressures reached inside a cavitation bubble containing nitrogen in water at ambient temperature and pressure before collapsing are nearly 4200 K and 975 bar, respectively. The high temperature existing inside cavitation bubbles accounts for radical formation, whereas the shock wave caused by bubble implosion may be responsible for the increased chemical reactivity.

Influence of Different Parameters on the Cavitation Process

The different processes occurring during cavitation (i.e. nucleation, bubble growth and collapse) can be affected by parameters such as liquid medium, intensity and hydrostatic pressure, which are among the most important.

Thus, the formation of cavitation bubbles decreases on increasing ultrasonic frequency. This is due to insufficient time for the rarefaction cycle to allow the growth of the bubble so that disruption of the liquid can be produced.

As expected, cavitation is decreased in viscous media as a result of the increased negative pressure in the rarefaction region needed for disruption of the liquid.

The number of nuclei for cavitation depends on temperature. An increase of temperature from -10 to $+50^\circ$C causes an increase in sonochemical effects as a result of the increased cavitation. Nevertheless,

when temperature exceeds 50°C the decrease in surface tension and increase in vapour pressure within the cavity will result in a lower P_{max} and, consequently, sonochemical effects will diminish.

The increase in gas content within the liquid leads to a lower cavitation threshold and intensity of the shock wave released on the collapse of the bubble. It has been observed that the use of monoatomic gases (He, Ar, Ne) provides more effective cavitation than diatomic gases (N_2, O_2, air).

External pressure also influences the cavitation process. Thus, when the external pressure is increased (P_h), a lower cavitation threshold and intensity of cavitational collapse are observed. When $P_h - P_a > 0$, it means that the negative phase of the sound will no longer exist, hence eliminating cavitation.

Finally, another factor that can influence cavitation is intensity, which enhances cavitation.

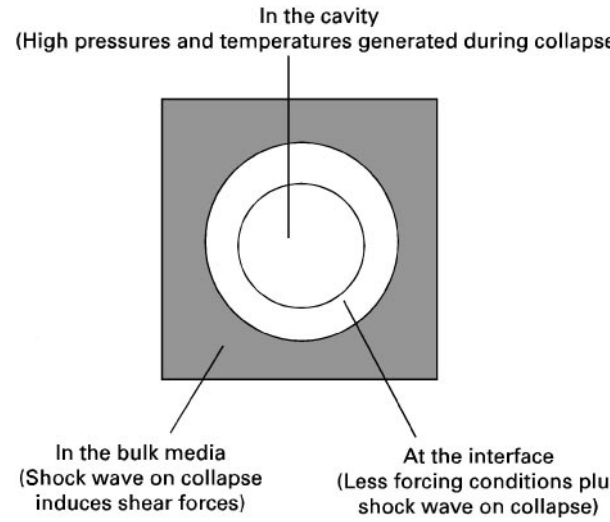
In the cavity
(High pressures and temperatures generated during collapse)
In the bulk media
(Shock wave on collapse induces shear forces)
At the interface
(Less forcing conditions plus shock wave on collapse)

Figure 3 Cavitation effects in a homogeneous liquid.

Effect of Power Ultrasound on Chemical Systems

Homogeneous Medium

Mechanical and chemical effects caused by cavitation fall into three different processes (**Figure 3**). First, the cavitation bubble contains solvent vapour which is subject to high temperatures and pressures on collapsing. This promotes the formation of reactive species, e.g. radicals. For example, when water is used as solvent the following reactions take place:

$$H_2O \rightarrow H\bullet + \bullet OH$$

$$H\bullet + OH\bullet \rightarrow H_2O$$

$$H\bullet + H\bullet \rightarrow H_2$$

$$OH\bullet + OH\bullet \rightarrow H_2O_2$$

$$H\bullet + O_2 \rightarrow HO_2\bullet$$

$$H\bullet + O_2 \rightarrow HO_2\bullet$$

$$H\bullet + HO_2\bullet \rightarrow H_2O_2$$

$$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2$$

$$H_2O + OH\bullet \rightarrow H_2O_2 + H\bullet$$

Second, surface-active reagents can accumulate at the interface between the bubble and the bulk liquid. Finally, in the surrounding of the bubble, an intense shock wave will be produced causing enormous shear forces.

Heterogeneous Medium

In this case, there are two types of cavitational collapse that can affect the surface of solids (**Figure 4**): (1) cavitational collapse on the surface of the solid due to the presence of surface defects,

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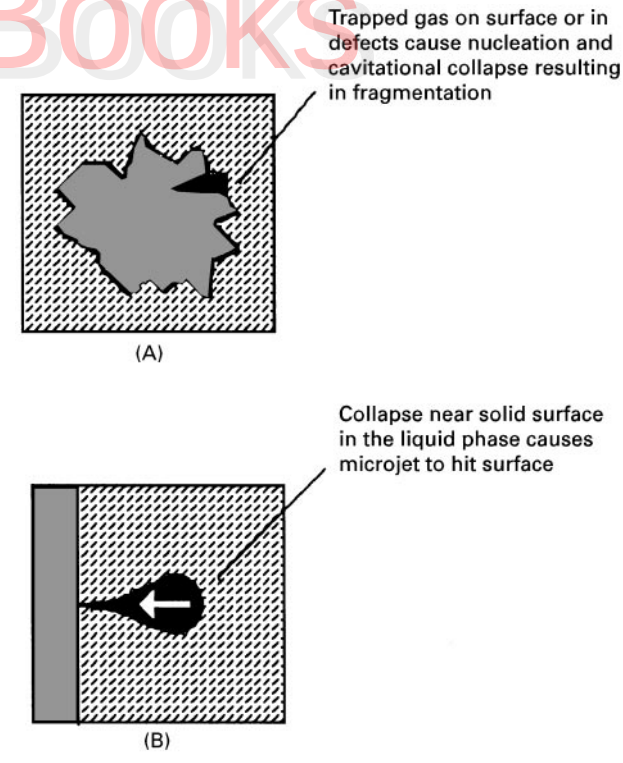
Trapped gas on surface or in defects cause nucleation and cavitational collapse resulting in fragmentation
(A)
Collapse near solid surface in the liquid phase causes microjet to hit surface
(B)

Figure 4 Cavitational effects at a solid–liquid interface: (A) cavitational collapse on the surface of a solid particle; (B) cavitational collapse close to a surface of a solid particle.

entrapped gases or impurities; (2) cavitational collapse close to a surface causing a microstreaming of solvent to impinge on the surface (i.e. cleaning action of ultrasound). It has been observed that ultrasonic irradiation can cause particle rupture (i.e. disruption) which results in a decrease in particle size and an increase in surface area for reaction. Alternatively, cavitational collapse in a medium containing two immiscible liquids can cause the formation of an emulsion.

Instrumentation

Among the several types of sonicator systems currently available, mostly bath and probe-type sonicators are used. Both systems are based on an electromagnetic transducer (i.e. device capable of converting mechanical or electrical energy into high frequency sound) as a source of ultrasound power, commonly operating at a fixed frequency of 20 kHz.

Ultrasonic sources used now rely on the piezoelectric effect discovered by Curie (1880). Ultrasonic processors implement transducers which are based on the changes in dimension of some materials on application of an electrical potential across opposite faces. When the potential is modulated at high frequency, the material converts the electrical energy into mechanical energy (sound). A sufficiently high alternating potential will result in the generation of ultrasound. The first ultrasonic transducer was reported by Galton in 1883, who tried to establish the threshold frequency of human hearing.

Bath Systems

In these systems the transducer is usually placed below a stainless steel tank, the base of which is the source of ultrasound (**Figure 5**). Some tanks are also provided with a thermostatically controlled heater. Typically, the ultrasound power levels delivered by most commercial ultrasonic baths (e.g., 1–5 W cm^{-2}) are sufficient for cleaning, degassing of solvents and extraction of adsorbed metals and organic pollutants from environmental samples, but are less effective for extraction of analytes bound to the matrix. The power should be great enough to cause cavitation within the extraction vessel placed inside the bath; this is not always achieved with commercial ultrasonic baths.

An important factor influencing extraction efficiency is the position of the extraction vessel inside the bath. For a bath with a single transducer on the base, the extraction vessel must be located just above the transducer, since power delivery will be a maximum at this position. In order to obtain reproducible results, the bath must be either thermostatted or preheated at the equilibrium temperature (i.e. maximum temperature measured in the liquid under continuous running conditions) since most cleaning baths warm up slowly during operation. An important drawback of most cleaning baths is the lack of power adjustment control.

Probe Systems

Probe-type sonicators are able to deliver to the extraction medium up to 100-fold greater power than that of an ultrasonic bath, so that a better performance is expected. One main feature for the successful application of ultrasonic probes for many chemical processes is that the ultrasonic energy is not transferred through the liquid medium to the extraction vessel but introduced directly into the system (**Figure 6**). The ultrasonic probe consists of the following components:

- A generator which is the source of alternating electrical frequency (typically 20 kHz). The generator allows tuning to be carried out for optimum performance.

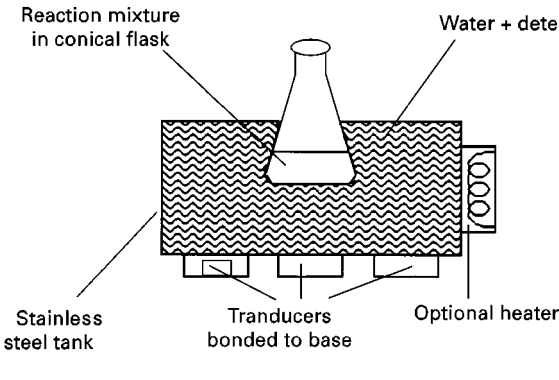

Figure 5 Schematic diagram of an ultrasonic bath.

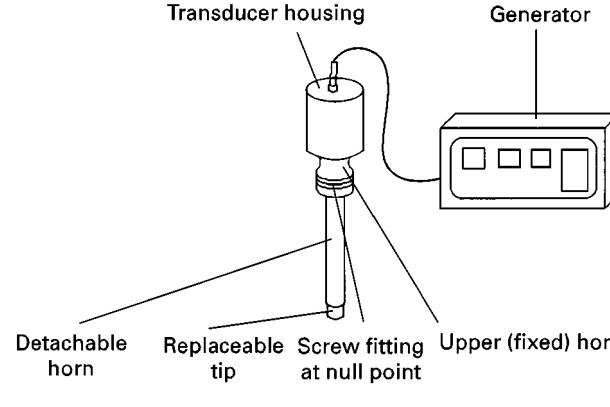

Figure 6 Schematic diagram of a probe-type sonicator.

- Ability of the ultrasonic processor to be used in pulsed mode operation which allows the medium to cool between pulses of sonication.
- The upper horn element – a piece of titanium to which the detachable horn is attached, forming both the emitter or booster.
- A detachable horn, usually made of a titanium alloy, which allows the vibration of the fixed horn to be transmitted to a chemical system. Tip erosion can occur as a result of cavitation. Depending on the volume of sample to be irradiated a range of detachable horns can be used.

Despite the improved performance displayed by probe-type sonicators for solid–liquid extraction compared with cleaning baths, a series of problems can arise with the use of these sonicators. Volatile components can be lost due to the 'degassing' effect of the ultrasound power. Ultrasound irradiation by means of probes is accompanied by a large amount of heat generated during operation, hence some cooling of the sonication vessel is required.

Ultrasound-Assisted Extraction

Extraction techniques are widely accepted as a prerequisite for analytical determination of both organic and inorganic analytes in a large variety of samples.

As a part of an analytical process, sample preparation is considered to be an essential step so that the entire process can be simplified. In this case, the ability of many analytical systems to handle liquid samples has brought about the development of separation methods which fulfil a main objective, i.e. to obtain quantitative analyte leaching from the solid matrix using a suitable solvent, with little or no matrix release, so that matrix effects can be kept to a minimum during the measurement steps. For speciation applications, a last condition of a solid–liquid extraction method must be the maintenance of the species integrity during treatment.

Table 1 shows the most relevant methods for treatment of solid samples based on analyte extraction. An important requirement of most techniques shown is that solvents at high temperature (i.e. at boiling point) or pressure must be used. In contrast, operation with ultrasonic processors can be performed at ambient temperature and normal pressure, and mild chemical conditions can be used in most cases.

Sonication is usually recommended for pretreatment of solid environmental samples for the extraction of nonvolatile and semivolatile organic compounds from solid, such as soils, sludges and wastes. When comparing the different methods available for analyte extraction from solid samples, sonication is considered as an effective method since unsophisticated instrumentation is required and solid–liquid separations can usually be performed in a short time using diluted reagents and low temperatures. To date, most of applications of ultrasonic extraction have been carried out for organic compounds, but the usefulness of ultrasound for element extraction is still to be explored. Some examples of solid–liquid extraction of some elements with the use of ultrasound are shown in **Table 2**. It should be pointed out that for many applications reported in this table, operation conditions were intended to obtain a homogeneous slurry so that a representative aliquot could be sampled; specific optimization of the variables influencing ultrasound-assisted extraction processes was not performed. Significant variables influencing the solid–liquid extraction process with a probe-type sonicator are sonication time, vibrational amplitude of the probe, acid concentration, particle size and solid concentration in the liquid. In general, the presence of an acidic liquid is an important prerequisite for quantitative extraction to be achieved; nitric acid at low concentration (e.g. 3–5% v/v) is usually chosen for extraction of elements from solid samples.

Quantitative extraction can be achieved for some analytes such as As, Cu, Pb, Cd, etc., from plant and animal tissues. Nevertheless, incomplete extraction has been observed from samples containing a typical inorganic matrix (e.g. sediment). It is believed that this finding is related to the ability of ultrasound to penetrate the solid material. A further variable that influences the solid–liquid extraction is the analyte–matrix interaction. Thus, strongly bound analytes should be more difficult to extract, thereby requiring more stringent extraction conditions. A relationship between extractability and binding characteristics of elements in the sample is yet to be established.

The extraction efficiency obtained with ultrasound could be increased by addition of glass beads which promote particle disruption by focusing the energy released by cavitation, and by physical crushing. Particle disruption could also be enhanced by increasing hydrostatic pressure and viscosity. The use of a bubbling gas during sonication gives rise to an enhanced formation of H_2O_2 and hydroxyl radicals ($OH\cdot$) thus aiding analyte extraction from oxidizable materials. In general, the use of probe-type sonicators at the appropriate vibrational amplitude and sonication time is required so that extraction efficiency can be improved for strongly-bound elements.

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Table 1 Extraction methods from solid samples.

Sample pretreatment method	*Principles of the technique*
Accelerated solvent	Sample is placed in a sealed container and heated to a temperature higher than its boiling point, causing pressure in the vessel to rise.
Automated Soxhlet	A combination of hot solvent leaching and Soxhlet extraction; sample in thimble is first immersed in boiling solvent and then the thimble is raised for Soxhlet extraction with solvent refluxing.
Forced-flow leaching	Sample is placed in a flow-through tube, and solvent is pumped or pushed through high-pressure nitrogen gas, while the tube is heated near the boiling point of solvent.
Gas phase	After equilibrium, analytes partition themselves between a gas phase and the solid phase at a constant ratio; with static headspace extraction, volatiles are sampled above the solid; with dynamic headspace extraction, volatiles are sampled by continuously purging the headspace above a sample with inert gas, trapping them on a solid medium, and then thermally desorbing them into a gas chromatograph.
Homogenization	Sample is placed in a blender, solvent is added, and sample is homogenized to a finely divided state; solvent is removed for further work-up.
Pervaporation	Volatile substances present in a heated donor phase placed inside a pervaporation module evaporate through a porous membrane and the vapour condenses on the surface of a cool acceptor stream on the other side of the membrane.
Solid–liquid extraction	Sample is shaken together with the appropriate solvent in a container and the liquid separated by filtration
Sonication	Finely divided sample in a container is immersed in ultrasonic bath with solvent and subjected to ultrasonic irradiation; an ultrasonic probe or cell disrupter can also be used.
Soxhlet extraction	Sample is placed in a disposable, porous container (thimble); constantly refluxing solvent flows through the thimble and leaches out analytes that are collected continuously.
Supercritical fluid	Sample is placed in flow-through container and a supercritical fluid (e.g. CO_2) is passed through sample; after depressurization, extracted analyte is collected in solvent or trapped on adsorbent and desorbed by rinsing with solvent.
Thermal	A form of dynamic headspace analysis, but the sample is heated (controlled) to much higher temperatures (as high as 350°C).

Contents based on Majors RE (1996) *LC-GC International*, 638 and Luque de Castro MD and Papaefstathiou I (1998) *Trends in Analytical Chemistry* 17: 41.

Future Prospects

The use of ultrasound as a sample preparation method for solid–liquid extraction is widespread in many laboratories and can be regarded as fast and effective. Extractions based on sonication have been employed for the isolation of weakly-bound organic compounds from solid samples such as soils, animal tissue, plants, etc., and are comparable to methods involving more intensive treatments (e.g., Soxhlet, accelerated solvent, etc.). However, ultrasound applied to solid–liquid extraction of inorganic analytes has rarely been attempted, perhaps owing to the inefficient sonochemical effects caused by most ultrasonic baths, which are more extended than probe-type sonicators. Ultrasound irradiation from high-intensity ultrasonic processors opens the door to new perspectives, mainly concerning those analytes that are strongly-bound to the matrix. Thus, extraction of elements from solid samples is feasible under optimized sonication conditions, hence avoiding the more intensive treatments commonly employed for matrix decomposition (i.e. dry or wet ashing procedures). New possibilities of ultrasound lie in its use as selective extraction techniques for metal speciation in conjunction with the appropriate leaching reagents. Thus, ultrasound-accelerated sequential extraction schemes for metal partitioning in environmental solid samples (e.g. soil, sediment, sewage sludge) or selective extraction of physicochemical forms of elements constitute new sample preparation strategies which deserve further research.

Table 2 Percentage of metal extracted into the liquid phase of slurries prepared in an acidic diluent and subsequently homogenized by sonication

Sample	*Element and percentage of extraction*	*Sonication system*	*Reference*
Bovine liver	Cd (111%)	Bath	1
Bovine liver	Mn (100%), Fe (72%)	Probe	2
Cabbage leave	Cd (89%), Pb (1%)	Probe	3
Cabbage root	Cd (86%), Pb (1.5%)	Probe	3
Carbon	Cr (14%)	Probe	4
Carbon	Cu (69%), Cr (2%)	Probe	5
Lemon leaves	Cd (67%), Cu (88%), Mn (98%)	Bath	1
Orchard leaves	Cd (100%), Cu (88%), Pb (98%)	Bath	1
Oyster	Cd (99%), Pb (98%)	Bath	6
Prawns	Se (88%)	Bath	6
Rice flour	Cd (100%)	Bath	1
Sediment	Cr (30%)	Probe	4
Sediment	Cu (60%), Cr (10%)	Probe	5
Silica gel	As (60%), Cr (65%), Ni (77%)	Probe	7
Spinach	Cu (98%), Cr (74%)	Probe	5
Spinach	Mn (100%), Zn (74%), Fe (36%), Cu (100%)	Probe	2
Talc	As (59%), Cr (61%), Ni (74%)	Probe	7
Tomato leaves	Mn (70%), Fe (70%), Cr (51%)	Probe	2
Tomato leaves	Mn (92%)	Bath	1
Wheat flour	Mn (97%), Fe (88%)	Probe	2

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See also: **III / Ultrasound-Assisted Metal Extractions.**

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